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Low-Pressure Mercury Arc for Ultraviolet Calibration

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A study was made of the visible-ultraviolet irradiance produced by a commercial low-pressure mercury arc operated by an accompanying power supply with a rated input of 115 volts ac. The 2537 Å irradiance was 3.9 μW/cm^2 at one meter at a specified axial position in ambient air at 20°C. The 2537 Å irradiance changed less than 2% when power-supply input varied from 105 to 130 volts ac, with environmental temperatures of 19.4°C and 26.8°C and ambient air flows of 11.2 and 14.7 cm/sec, respectively. Spectral analysis of the lamp irradiance in the 1900–6000 Å range showed that 92% originated from the 2537 Å mercury resonance line while the remaining 8% is attributable to 12 other mercury lines. The intensities of 55 other spectral lines of negligible intensity in the investigated range are given relative to the intensity of the 2537 Å line. The experimental mean free path of electrons in mercury vapor at 1 mm of Hg and 273°K was $\sim 5 \times 10^{-3}$ cm whereas kinetic theory gave 6.7×10^{-3} cm.

I. Introduction

The 2537 Å resonance line of mercury provides a useful source of ultraviolet for calibration in studies of photochemical reactions and photoelectric effects. One of the problems with any lamp using mercury, as well as with other gas discharge lamps, is the variation of irradiance with lamp current and environmental changes such as temperature and air flow. There is consequently a need for an ultraviolet lamp whose irradiance of several microwatts/cm^2 can be established as "stable" over a "large" current range and whose construction makes it a convenient laboratory instrument. Such a lamp is the commercially available "Pen-Ray Lamp"* whose characteristics are reported in this paper.

The Pen-Ray lamp produces a low-pressure mercury arc contained in a septum quartz tube with approximate length of 52 mm and diameter of 6.5 mm. It is operated by a special power supply with rated input of 115 volts, 60 cycles.† A metal cap, with a 1-mm aperture, accompanies the lamp.

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* Model 11 SC-1, Black Light Eastern Corporation, Port Washington, Long Island, N.Y.

† Model SCT-1 Power-Supply, Black Light Eastern Corporation.

II. Experimental Conditions

Calibration of the 2537 Å radiation of the Pen-Ray lamp employed a General Electric Ultraviolet Intensity Meter.[1] Verification of the ultraviolet meter calibration for 2537 Å is discussed in the following section.

The lamp current and voltage were monitored during calibration as was the lamp power-supply input voltage furnished by an electronic ac voltage regulator stabilized for twenty-four hours.

All data were acquired in an environment of 24–25°C unless otherwise stated.

III. Ultraviolet Meter Calibration

The ultraviolet meter 2537 Å calibration was verified by comparing its 2537 Å measurements with those of a tantalum cell at the National Bureau of Standards[2] (NBS.) and a gold-black Golay cell in these Laboratories.[3] In all measurements with the ultraviolet meter its aperture was on the ×1 scale. The lamps used for this comparison were apertured GE type G4T4/1 operated at 75 mA.

Comparison with the tantalum-cell measurements required the use of a neutral-density filter and a broad-band 2537 Å interference filter. The ultraviolet meter flux values, corrected for the filters, and those of the tantalum cell for two mercury arcs are shown in Table I.

Comparison with the Golay cell, which used the same interference filter, was made after the Golay cell sensitivity was determined with a carbon lamp calibrated by NBS. Flux values for three mercury lamps were obtained with the Golay cell and the ultraviolet meter. These filter-corrected values are contained in Table II.

Table I. Calibration of 2537 Å Intensity of Mercury Lamps at 20 cm

	Microwatts of 2537 Å per cm² at 20 cm	
Lamp[a]	Tantalum cell	UV meter
1	—	—
2	48.4	46.2 ± 2.4
3	49.4	46.2 ± 2.4

[a] Lamp No. 1 has been used considerably; consequently, because its radiation has decreased since tantalum-cell calibration, it is not used as a tantalum-cell comparison.

Table II. Calibration of 2537 Å Intensity of Mercury Lamps at 1 m

	Microwatts of 2537 Å per cm² at 1 m	
Lamp	Golay cell	UV meter
1	1.42	1.46 ± 0.08
2	2.02	2.02 ± 0.10
3	2.02	2.02 ± 0.10

The ultraviolet meter was observed to be insensitive to fluorescent lights because of the spectral response of the cadmium cell used in the meter as well as the transmittance of glass used in fluorescent lights. This insensitivity to room light was first observed by Taylor and Haynes.[1]

Mercury-lamp calibrations by the ultraviolet meter were the same with or without the interference filter which means that wavelengths of about 3000 Å and longer can be neglected in their contributions to the ultraviolet meter readings. This lack of effect on calibration is likewise due to cadmium spectral response combined with relative spectral intensities of low-pressure mercury arcs.

The agreement in flux measurements among the ultraviolet meter, tantalum cell, and Golay cell was the basis for the conclusion that the precision of the 2537 Å calibration with the ultraviolet meter was limited by ability to read the meter, with a maximum accuracy of 2%.

IV. Radial Distribution of Radiation

Since the lamp capillary appeared to be elliptical in cross section, it seemed probable that this difference should result in irradiance varying with radial position. The variation of irradiance with radial position was therefore determined by aligning the lamp length and ultraviolet meter parallel and measuring the energy as the lamp was rotated, marking the lamp for zero degrees at a position of minimum flux. The lamp current was set at 16 mA.

The variation in irradiance, shown in Fig. 1, is that to be expected from the lamp-wall geometry. There are positions of minimum and maximum irradiance which repeat at 180°. For calibration purposes, these results assisted in determining the angle for which there is the smallest percentage irradiance change over a small range, such as plus or minus ten degrees.

Additional calibrations were made with the lamp at a position near maximum output. This position corresponds to an angle of 290° in Fig. 1.

V. Calibration and Electrical Properties

One of the purposes of this study was to determine the effect of small changes in power-supply input voltage on the 2537 Å irradiance. This purpose was accomplished by using the ultraviolet meter at 1 meter and by covering its entrance window with the interference filter used to calibrate the ultraviolet meter. The procedure was to increase the power-supply input potential from zero to the minimum at which the lamp would operate, approximately 30 volts. After five minutes, the minimum potential for operation dropped to 21 volts. Following lamp operation at this power-supply input voltage, irradiance measurements were made at the end of two five-minute periods. The input voltage was then increased by 10 volts and again measurements were made at the end of two five-minute periods.

The 2537 Å irradiance did not change detectably from the end of the first five-minute period to the end

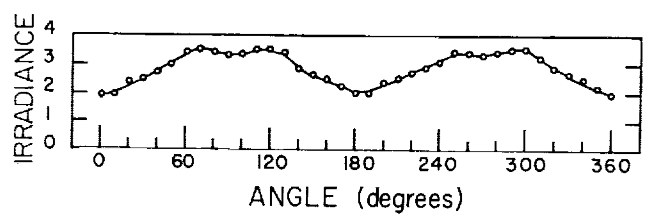

Fig. 1. Radial distribution of 2537 Å irradiance (μW/cm² at 1 meter with lamp current 16 mA). Position of minimum irradiance designated as zero degrees.

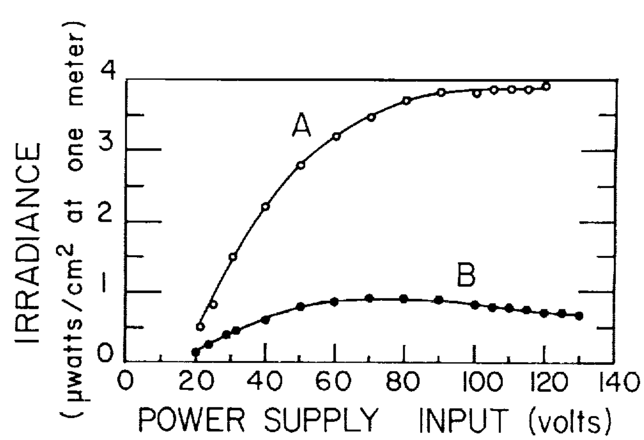

Fig. 2. Lamp 2537 Å irradiance as a function of power-supply input. Curve A is for the lamp and curve B is for the central area as described in Section V.

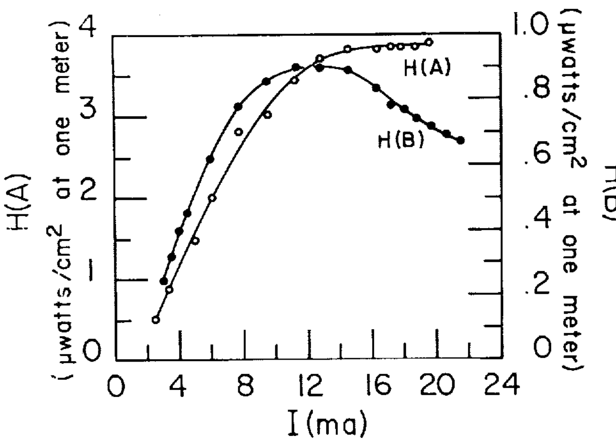

Fig. 3. The 2537 Å irradiance of the lamp $H(A)$ and central area $H(B)$ as functions of lamp current.

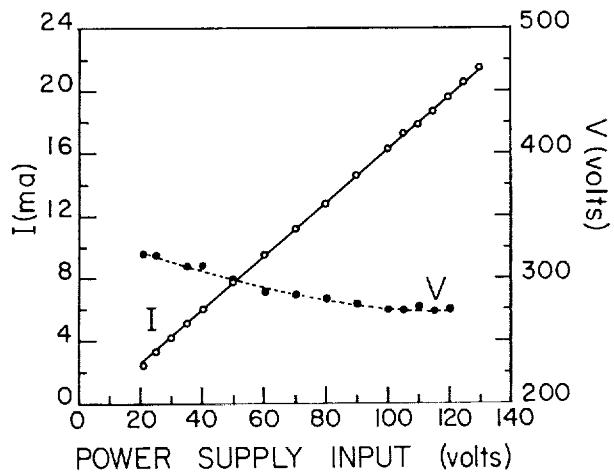

Fig. 4. Lamp current I and lamp potential V vs lamp power-supply input.

of the second five-minute period when the voltage was increased; however, when going from a higher input voltage to a lower one, it appeared that at least ten minutes were required to establish thermal equilibrium.

After the irradiance characteristics were determined, a restricted central area of the arc was selected for calibration by milling along the lamp-cap diameter an aperture with a length of 12 mm. The aperture was rotated so that its center corresponded to the position of maximum lamp output and permitted reproducible attainment of a selected area of the lamp. Data obtained with this cap on the lamp are referred to as that of the central area.

In Fig. 2 is shown the calibration for the lamp and also for the central area. Similar calibrations as functions of lamp current are contained in Fig. 3.

Lamp current was found to be a linear function of the power-supply input voltage as shown in Fig. 4, and this relation indicates that lamp current is determined by the transformer in the lamp power supply. Lamp potential is also shown in Fig. 4.

VI. Environmental Temperature Effect on Irradiance

The lamp irradiance was determined in two "typical" laboratories with ambient air flows of 11.2 and 14.7 cm/sec and respective temperatures of 19.4°C and 26.8°C. The irradiance remained constant for these two temperatures and air flows. Under these same conditions, the irradiance changed not more than two percent with power supply input voltages between 105 and 130 volts, as shown in Fig. 5.

VII. Lamp Temperature

A thermistor, mounted in contact with the surface opposite that being calibrated, was used to measure lamp temperature when operated in ambient air at 11.2 cm/sec and 24°C. Correlation of input voltage with lamp temperature can be seen in Fig. 6. Although these measurements pertain only to the lamp, some indication of the effect of the metal cap, used for central-area isolation, was obtained from a bulb-

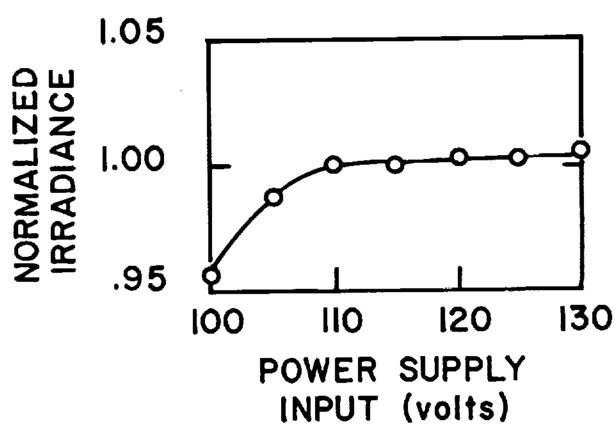

Fig. 5. Normalized lamp 2537 Å irradiance in environments of 19.4°C and 26.8°C with ambient air flow of 11.2 and 14.7 cm/sec, respectively. With a specific power-supply input, the irradiance was the same for each of these two sets of conditions.

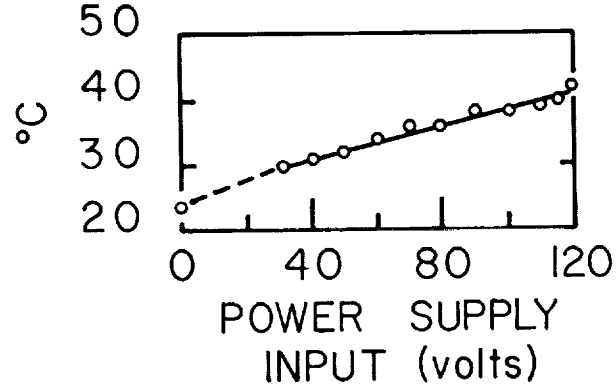

Fig. 6. Lamp envelope temperature as a function of power-supply input.

thermometer reading taken on the cap-top when the lamp was operating at 17.0 mA. This temperature was 10°C higher than that observed when the lamp was operating without the cap.

VIII. Spectral Distribution of Radiation

Of primary importance for any specific wavelength calibration of a nondispersed source is the assurance that all other wavelengths are truly negligible. To determine whether or not such conditions existed during the Pen-Ray lamp 2537 Å calibrations, it was necessary to resolve the lamp spectrum by using a spectrophotometer and a radiance-standard lamp.[4]

The Pen-Ray lamp and radiance-standard lamp were independently substituted for the hydrogen arc in the Cary Recording Spectrophotometer Model 14 P.M. In the sample chamber of the spectrophotometer a front-surfaced aluminum mirror reflected the beam 90° to the top of the chamber, permitting the spectrophotometer to be used as a monochromator. On top of the chamber a cover with a 1.5-cm-diameter aperture permitted the beam to enter the detector.

The detector was the E.M.I. 6256B photomultiplier with a 10-mm-diameter cathode on a quartz faceplate. The voltage was set at the minimum required for adequate recording of the Pen-Ray lamp continuum: a potential of 1200 volts, equally divided among the 13 dynodes, provided sufficient photomultiplier gain to record the weak continuum as 0.35×10^{-9} A in the 1950 Å region and 1.50×10^{-9} A in the 5860 Å region, with a dark current less than 10^{-10} A.

To avoid photomultiplier fatigue when a line intensity provided a detector signal greater than 10^{-6} A, a record was made of that region, with the line intensity being determined in another scan during which the detector was operated at either 600 volts or 800 volts. Signals thus obtained were normalized to those of 1200 volts by applying the voltage-gain relationships obtained during the experiment.

When using the standard lamp as the light source of the Cary Model 14, the detector potential was adjusted to provide a signal of approximately 10^{-8} A at 2500 Å, with a decrease in potential when the signal at other wavelengths approached 10^{-6} A. Gain-potential relations were obtained during the experiment and current values were normalized to those at the same potential used for obtaining the 2500 Å signal. Potential was constantly monitored with electrostatic voltmeters with ½% full scale accuracies.

The spectrophotometer had the same slit width and scan rate for both the Pen-Ray and standard lamp, with the standard lamp being operated at 35 A for which it was calibrated. Since the same detector and related equipment were used throughout these experiments, the relative intensities of lines were determined from the detector signals, assuming the standard-lamp irradiance is a continuous function of wavelength, as is expected of the tungsten ribbon which approximates a gray body. With these conditions, the ratio of irradiances H_1 and H_2 of wavelengths λ_1 and λ_2, respectively, will be

$$\frac{H_1}{H_2} = \frac{I_1}{I_2}\frac{I'_2}{I'_1}\frac{H'_1}{H'_2}, \tag{1}$$

where

I_1, I_2 = detector signal current obtained with λ_1 and λ_2 with Pen-Ray lamp,
I'_1, I'_2 = detector signal current obtained with λ_1 and λ_2 with standard lamp,
H'_1, H'_2 = calibrated irradiance of λ_1 and λ_2 of standard lamp.

Detector signal currents were corrected for experimental effective bandwidths.

The Pen-Ray lamp spectrum was obtained in the 6000–1900 Å range for the lamp operating at 5.0 mA and again at 16.0 mA. Since the relative intensities of the twenty most prominent lines did not change for the two currents, only relative intensities of lines observed with the lamp operating at 16.0 mA are reported in Table III for the 2500–6000 Å range.

Since Eq. (1) is valid only for the standard-lamp calibration range of 2500–7500 Å, relative intensities from 1900 to 2500 Å were obtained by using the photomultiplier experimental relative quantum yield (electrons/photon) for 1900–2500 Å. The relative line intensities so measured are given in Table IV; however, since these values include monochromator attenuation, they represent lower limits of the relative intensities.

Table III. Wavelength Intensities Relative to 2537 Å

Å	Relative intensity	Å	Relative intensity
2537	1.0	3591	2.1×10^{-7}
2575	6.0×10^{-5}	3650	8.9×10^{-3}
2603	2.0×10^{-6}	3655	2.1×10^{-3}
2640	7.4×10^{-6}	3663	1.4×10^{-3}
2653	1.1×10^{-3}	3705	1.3×10^{-6}
2676	1.8×10^{-6}	3801	5.0×10^{-7}
2700	3.0×10^{-5}	3900	2.4×10^{-6}
2753	3.2×10^{-4}	3906	8.2×10^{-6}
2779	7.5×10^{-6}	3984	1.1×10^{-6}
2794	1.6×10^{-6}	4047	8.9×10^{-3}
2802	1.7×10^{-4}	4078	5.5×10^{-4}
2813	4.4×10^{-5}	4106	2.4×10^{-6}
2821	1.0×10^{-4}	4157	4.4×10^{-7}
2828	1.2×10^{-4}	4200	6.5×10^{-7}
2856	1.2×10^{-5}	4259	2.2×10^{-7}
2894	7.9×10^{-4}	4358	1.7×10^{-2}
2925	5.2×10^{-5}	5026	6.3×10^{-7}
2965	6.0×10^{-3}	5354	2.7×10^{-7}
3022	1.1×10^{-2}	5461	1.2×10^{-2}
3126	7.1×10^{-3}	5676	5.0×10^{-7}
3132	1.1×10^{-2}	5770	1.7×10^{-3}
3341	5.5×10^{-4}	5790	1.8×10^{-3}
3524	5.9×10^{-8}		

Table IV. Wavelength Intensities Relative to 2537 Å[a]

Å	Relative intensity
1942	1.7×10^{-5}
2027	4.9×10^{-7}
2053	4.3×10^{-6}
2232	3.0×10^{-7}
2260	1.6×10^{-6}
2262	8.6×10^{-6}
2270	2.0×10^{-7}
2280	2.2×10^{-7}
2285	4.8×10^{-7}
2290	2.2×10^{-7}
2304	5.2×10^{-6}
2314	7.9×10^{-8}
2324	1.0×10^{-6}
2342	3.9×10^{-7}
2346	3.2×10^{-6}
2354	3.9×10^{-6}
2366	1.2×10^{-7}
2379	3.3×10^{-5}
2400	1.6×10^{-5}
2448	6.0×10^{-6}
2459	4.2×10^{-7}
2466	1.8×10^{-5}
2483	2.3×10^{-4}
2537	1.0

[a] These relative intensities include monochromator attenuation and hence are the lower limit of relative intensities in air.

It was not possible to compare wavelength relative intensities of this study with those of other investigators because of differences in methods of obtaining relative intensities.[5–11]

IX. Electron Mean Free Path

In their investigation of low-pressure mercury arcs (1.8×10^{-4} to 5.3×10^{-3} mm of Hg), Duffendack and Koppius[9] derived an expression for the arbitrary intensity e^J of wavelength J in an arc with current i:

$$e^J = B\, i\, (1 - e^{-ap}), \tag{2}$$

where

B = a constant,
p = pressure in mm of Hg,
a = d/λ_E,
d = arc length in cm,
λ_E = electron mean free path (cm) in mercury vapor at 273°K and a pressure of 1 mm of Hg.

Equation (2) was fitted to their experimental data, with B and a varying for each wavelength investigated. Whereas a should have remained constant, their experimental values ranged from 0.10×10^4 to 0.24×10^4. For their eight a values, the average λ_E was 1.9×10^{-3} cm.

The Pen-Ray lamp irradiance $H(A)$ in Fig. 2 indicated that it could be fitted to an expression similar to Eq. (2), and it was assumed that $H(A)_V$ for power-supply input V was of the form

$$H(A)_V = K(1 - e^{-ap}), \tag{3}$$

where K is a constant, and a and p are the same as in Eq. (2) but p is now to be expressed as a function of V.

It was shown in Fig. 6 that lamp temperature T is a linear function of V; hence, since $\log_e p$ is a linear function of T over the 25–46°C range,[12] we may approximate p by fitting the curves of Fig. 6 and the cited p vs T data. After determining the constants, we find

$$p \text{ (mm of Hg)} \sim e^{(1.0 \times 10^{-2} V - 5.41)}. \tag{4}$$

Equation (4) was substituted into Eq. (3) and the ratio of irradiances for $V = 60$ volts and $V = 120$ volts was used to calculate a. The experimental a thus determined was 2.1×10^2 per mm of Hg. This a was then used in Eq. (3) and found to fit the experimental data to within 10% at $V = 50$ volts and 5% for $V \geqslant 80$ volts. However, it does not provide the detail of Fig. 5. For $V \leqslant 40$ volts, the experimental a value gives $H(A)_V$ much greater values than those in Fig. 2. Considering that the approximations used in determining a entered into a second exponent, the data fitting for $V \geqslant 50$ volts is as good as can be expected.

The arc length in the Pen-Ray lamp is about 10 cm, and from $a \sim 2.1 \times 10^2$ we find

$$\lambda_E \sim 5 \times 10^{-3} \text{ cm}.$$

Kinetic theory for the Maxwell distribution of molecules, as shown by Jeans,[13] gives the mean free path as

$$\lambda_E = \frac{1}{\sqrt{2}\, \pi \gamma \sigma^2}, \tag{5}$$

where

γ = number of molecules per unit volume,
σ = diameter of molecule.

Jeans noted that in electron–molecule collisions, the value of σ is very nearly the radius of the molecule. We assume that for electrons in mercury vapor σ is the radius of the mercury molecule, 3.13×10^{-8} cm.[14] For mercury at a pressure of 1 mm of Hg and 273°K the electron mean free path is

$$\lambda_E = 6.7 \times 10^{-3} \text{ cm}.$$

The agreement of the Pen-Ray lamp λ_E with that calculated by kinetic theory implies that the assumption of Eq. (3) is valid. Although it is known that λ_E varies with electron energy,[5–8,10,11,15–17] the approximations in obtaining λ_E prevent any reliable quantitative comparison with other studies.

Equation (2) contains the constant B which is related to ionization probability and was constant during the experiments by Duffendack and Koppius.[9] For the Pen-Ray lamp, however, B must be changing with power-supply input V as the potential across the lamp V_L decreased with increasing V, with V_L being ~ 273 volts for $V \geqslant 100$ volts. Since the lamp was operated with ac voltage, the electrons have an energy distribution as a function of time and therefore the Pen-Ray lamp λ_E represents the average mean free path of this distribution.

A more accurate determination of lamp temperature, potential, and electron temperature would assist in understanding the variation of B and λ_E with electron energy.

Equation (3) does not fit the data for the central area irradiance because for Eq. (3) it was assumed that the mercury vapor was an ideal gas with uniform temperature. Such a condition obviously does not exist, as the metal cap on the lamp causes a temperature gradient at the aperture. Other factors also probably contribute to the central area irradiance decrease at $V > 80$ volts.

X. Discussion

Before evaluating the use of the Pen-Ray lamp as a calibrated 2537 Å source, one should note that good agreement has been attained in 2537 Å intensity measurements with the ultraviolet meter, the tantalum cell at NBS, and the gold-black Golay cell in these Laboratories. Since the General Electric Company, in setting the ultraviolet meter sensitivity, used a secondary standard compared with a primary standard calibrated by NBS, and since the Golay cell sensitivity is determined by a carbon lamp calibrated by NBS, it is encouraging that consistency has been maintained throughout the various calibration methods.

This study yielded relative line intensities which are about one-tenth those published by the lamp manufacturer. This difference must include an estimated error of 10% in our relative-intensity measurements.

The 2537 Å irradiance was 3.9 μW/cm^2 at 1 meter with power-supply inputs between 105 and 130 volts ac.

The 2537 Å line comprised 92% of the total irradiance, and 12 other lines comprised the remaining 8%.

Future investigation of the lamp should determine the flux stability of the 2537 Å irradiance with operating time, as this investigation found no detectable decrease after sixteen hours of continuous operation at a current of 16 mA.

XI. Conclusion

The Pen-Ray lamp study shows that the lamp can serve as a calibrated 2537 Å source, and taken as a whole, it possesses the useful characteristic of uniform radiation intensity, within 2%, even when its power-supply input potential varies between 110 and 130 volts and environmental temperatures vary from 19.4 to 26.8°C, with ambient air flow from 11.2 to 14.7 cm/sec. Although this is not true for the central area alone as obtained with the described metal cap, a stable radiation intensity from this area can be obtained for a similar range of line voltages by limiting the lamp current to some value between 11 and 15 mA. With a ballast resistor to limit the lamp current to the 13 mA region, the capped lamp output will be stable for line-potential variations of approximately ten volts. When operated at this current the life of the lamp will probably be longer.

Five lamps were investigated and found to have similar characteristics shown in Figs. 1 through 6, and these characteristics were independent of the power supply. This latter observation indicates uniformity in the three power supplies used during these experiments.

When positioned at 290° as in Fig. 1, all lamps had irradiances within 10% of 3.9 μW/cm^2 at 1 meter in 11.2–14.7 cm/sec ambient air at 19.4–26.8°C. Although these air-flow and temperature ranges include conditions expected in a "typical" laboratory, each lamp should be calibrated before it is used as a calibrated source.

The author would like to thank Ralph Stair of the National Bureau of Standards and Steven C. Hardy of these Laboratories (now at National Bureau of Standards, Washington, D.C.) for their calibrations of the three secondary standard mercury arcs.

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